



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 927 748 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
07.07.1999 Bulletin 1999/27

(51) Int Cl.<sup>6</sup>: **C09C 1/42**, C09C 3/12,  
C08K 9/06

(21) Application number: **98310402.7**

(22) Date of filing: **17.12.1998**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

• **Thomas, Bryan**  
**Barry, Wales (GB)**

(30) Priority: **18.12.1997 GB 9726636**

(71) Applicant: **Dow Corning Corporation**  
**Midland, Michigan 48611 (US)**

(74) Representative: **Bullows, Michael**  
**Dow Corning Limited,**  
**Patent Department,**  
**Cardiff Road**  
**Barry CF63 2YL, Wales (GB)**

(72) Inventors:  
• **Joseph, Julie**  
**Bryncoch, Neath SA10 7SJ (GB)**

Remarks:

The application is published incomplete as filed  
(Article 93 (2) EPC).

(54) **Method for preparing hydrophobic clay**

(57) A method for the preparation of a hydrophobic clay by contacting an aqueous suspension of the clay with an organosilane of formula  $R^1_nSiX_{4-n}$  or an organosiloxane comprising units of formula  $R^2_nSiO_{(4-n)/2}$  in

the presence of an acid and a water-miscible solvent. The resulting clay suspension is then contacted with a water-immiscible solvent to effect separation of the hydrophobed clay from the suspension.

EP 0 927 748 A1

## Description

[0001] The present invention relates to the preparation of a hydrophobic clay, in particular the preparation of a hydrophobic clay by treatment thereof with an organosilicon compound.

[0002] Hydrophobic precipitated clay is useful as a reinforcing and/or extending filler in natural or synthetic rubbers and plastics, especially for applications where moisture sensitivity is a problem, for example cable and wire coatings, and is particularly useful as a reinforcing filler in silicone rubber compositions. Silicone rubbers formed mainly from cured polydiorganosiloxane fluids or gums alone generally have low elongation and tensile strength values; however, these physical properties may be improved by incorporating a reinforcing filler into the fluid or gum prior to curing.

[0003] A problem with using untreated clay filler as an ingredient for silicone rubber compositions, as well as with other fillers commonly employed in silicone rubber compositions, for example fumed and precipitated silica, is a tendency to interact with the polydiorganosiloxane fluid or gum causing a phenomenon typically referred to as "crepe hardening". Much effort has been made to treat the surface of reinforcing fillers with organosilanes or organosiloxanes to render the surface hydrophobic, reduce or diminish the tendency of the compositions to crepe harden, and thus improve the physical properties of the cured silicone rubber.

[0004] For example, U.S. Patent Number 3,015,645 teaches the preparation of hydrophobic silica powders by reacting an organosilicon compound such as dimethyldichlorosilane or trimethylmethoxysilane with a silica organogel in the presence of an acidic catalyst to form a hydrophobic silica hydrogel. The hydrophobic silica hydrogel is contacted with a water-immiscible organic solvent to convert the hydrophobic silica hydrogel to a hydrophobic silica organogel which segregates into the organic phase.

[0005] U.S. Patent Number 4,072,796 describes a method in which finely divided hydrophobic silica and silicates are prepared by precipitating alkali silicate solutions with mineral acids or metal salt solutions and treated with organohalosilanes selected from prepolycondensed organohalosilane and a mixture of prepolycondensed organohalosilanes.

[0006] U.S. Patent Number 5,009,874 describes a method for making a hydrophobic precipitated silica useful as a reinforcing filler in silicone elastomers. An organosilicon compound is added to a suspension of the precipitated silica to hydrophobe the silica, followed by addition of a water-immiscible organic solvent to separate the hydrophobic precipitated silica from the aqueous phase.

[0007] According to the present invention there is provided a method for preparing a hydrophobic clay, which method comprises:

(A) allowing a clay to be rendered hydrophobic by contacting an aqueous suspension of the clay with an organosilicon compound in the presence of an acid and a water-miscible solvent, wherein the organosilicon compound is selected from (i) organosilanes of formula  $R^1_a SiX_{4-a}$  wherein each  $R^1$  is independently selected from hydrogen and optionally substituted hydrocarbon radicals having 1 to 12 carbon atoms, each X is independently selected from halogen and alkoxy radicals having 1 to 12 carbon atoms, and  $a=1, 2, \text{ or } 3$ , and (ii) organosiloxanes comprising units of formula  $R^2_n SiO_{(4-n)/2}$  wherein each  $R^2$  is independently selected from hydrogen, hydroxy, and hydrocarbon radicals having 1 to 12 carbon atoms, at least 50 mole percent of the  $R^2$  substituents being hydrocarbon radicals, and  $n$  is 2 or 3, and

(B) contacting the clay suspension formed in step (A) with a water-immiscible solvent to effect separation of the hydrophobed clay from the suspension.

[0008] In step (A) of the present invention an aqueous suspension of a clay is hydrophobed with an organosilicon compound. Herein "clay" is given its dictionary definition, i.e. it refers to various forms of hydrated aluminosilicate, e.g. those hydrated aluminosilicates of general formula  $Al_2O_3 \cdot SiO_2 \cdot xH_2O$ , where  $x$  is the degree of hydration. Commonly known examples of clays include Fuller's Earth, bentonite, kaolin (China clay) and diatomite. A preferred clay for use in the present invention is kaolin, for example comprising approximately 50% by weight  $Al_2O_3$  and approximately 40-45% by weight  $SiO_2$ .

[0009] Preferred clays for use in the present invention have an average particle size of  $10\mu m$  or less, more preferably less than  $2\mu m$ . If desired, the clay may be subjected to a shearing force to reduce aggregate particle size and to improve the uniformity of the particle size distribution, prior to conduct of the present method. The shearing force may be applied, for example, by a mechanical means such as a high-speed mixer or by ultrasound.

[0010] The BET surface area of the clay used in the present method is not critical and may typically be from, for example,  $5m^2/g$  to  $20m^2/g$ . Preferred kaolin clays for use in the present method have a BET surface area from  $8m^2/g$  to  $16m^2/g$ .

[0011] Both calcined and uncalcined clays may be used in the present invention, although the former are preferred; calcination removes hydroxyl groups as water from the surface of the clay reducing hydrogen-bonding on the surface between hydroxyl groups thus leaving isolated hydroxyl groups available for reaction with the organosilicon compound.

Typical calcination temperatures for clays are 750°C and above.

**[0012]** The clay is present in step (A) of the present method in aqueous suspension. The amount of clay in the aqueous suspension is not critical and may be in a range of from 5 to 90 weight percent, more preferably from 10 to 50 weight percent, even more preferably from 10 to 30 weight percent.

**[0013]** The aqueous suspension of the clay is contacted with the organosilicon compound in the presence of a water-miscible solvent to facilitate the reaction of the organosilicon compound with the precipitated silica. Suitable water-miscible solvents include tetrahydrofuran and alcohols such as ethanol and isopropanol, with isopropanol being preferred.

**[0014]** The clay is treated with one or more organosilicon compounds selected from (i) and (ii) described above. For the organosilanes (i) of formula  $R^1_nSiX_{4-n}$ , each  $R^1$  is independently selected from hydrogen and optionally substituted hydrocarbon radicals having 1 to 12 carbon atoms. For example,  $R^1$  may be a monovalent hydrocarbon radical which is saturated or unsaturated, and/or which is substituted or unsubstituted. Each  $R^1$  may be, for example, an alkyl radical such as methyl, ethyl, propyl, t-butyl, hexyl, heptyl, octyl, decyl, and dodecyl; an alkenyl radical such as vinyl, allyl, and hexenyl; or an aryl radical such as phenyl, naphthyl, and tolyl. When the organosilane (i) contains X as either a halogen or an alkoxy group  $R^1$  may be substituted by one or more halogen atoms, for example  $R^1$  may be a halogen substituted alkyl radical such as chloromethyl, 3,3,3-trifluoropropyl, and 6-chlorohexyl, and  $R^1$  may contain a heteroatom in the hydrocarbon chain, for example to form a disulphide or polysulphide group. When the organosilane (i) contains X only as an alkoxy group  $R^1$  may also be organofunctional substituted, for example by mercapto, amino, carboxylic acid, ester or amido groups. Each  $R^1$  is preferably an alkyl radical. Each X in the above formula is independently selected from halogen and alkoxy radicals having 1 to 12 carbon atoms. As a halogen X is preferably chlorine. As an alkoxy radical X may be, for example, methoxy, ethoxy, and propoxy, preferably methoxy or ethoxy.

**[0015]** For the organosiloxanes (ii) comprising units of formula  $R^2_nSiO_{(4-n)/2}$ , each  $R^2$  is independently selected from hydrogen, hydroxy, and hydrocarbon radicals having 1 to 12 carbon atoms, at least 50 mole percent of the  $R^2$  substituents being hydrocarbon radicals, preferably methyl groups. For example,  $R^2$  may be an alkyl, alkenyl or aryl group as described above for  $R^1$ . The organosiloxanes (ii) can be linear or cyclic, and their viscosity can range from that of a fluid to a gum.

**[0016]** Suitable organosilicon compounds include diethyldichlorosilane, allylmethyldichlorosilane, methylphenyldichlorosilane, phenylethyldiethoxysilane, 3,3,3-trifluoropropylmethyldichlorosilane, trimethylbutoxysilane, n-octyltriethoxysilane, sym-diphenyltetramethyldisiloxane, trivinyltrimethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethyldisiloxane, pentylmethyldichlorosilane, divinylidipropoxysilane, vinylidimethylchlorosilane, vinylmethyldichlorosilane, vinylidimethylmethoxysilane, trimethylchlorosilane, hexamethyldisiloxane, hexenylmethyldichlorosilane, hexenyldimethylchlorosilane, dimethylchlorosilane, dimethyldichlorosilane, mercaptopropylmethyldimethoxysilane, bis(3-(triethoxysilyl)propyl)tetrasulfide, polydimethylcyclosiloxanes and polymethylhydrogencyclosiloxanes comprising 3 to about 20 dimethylsiloxy units and preferably 3 to about 7 dimethylsiloxy units, and trimethylsiloxy, hydroxydimethylsiloxy or chlorodimethyl endblocked polydimethylsiloxane or polymethylhydrogensiloxane polymers having a viscosity within a range of about 1 mPa.s to 1,000 mPa.s at 25°C. Preferred examples of organosilanes (i) for use in the present invention include dimethyldichlorosilane and n-octyltriethoxysilane, and preferred examples of organosiloxanes (ii) include  $(Me_2SiO)_4$ ,  $(MeHSiO)_4$ ,  $Me_3SiO(MeHSiO)_2SiMe_3$  and  $HO(Me_2SiO)_yH$ , wherein Me is methyl, z has an average value from 20 to 50 and y has an average value of from 10 to 15.

**[0017]** The organosilicon compound is added to adequately hydrophobe the clay, and is typically added in an amount of from 25 to 75 weight percent of the clay. An upper limit for the amount of organosilicon compound added is not critical since any amount in excess of the amount required for saturation treatment of the clay may act as a solvent in the present method, although preferably the amount of organosilicon compound added will be sufficient to treat the clay but not cause flocculation.

**[0018]** In step (A) of the present invention the aqueous suspension of the clay is contacted with one or more of the organosilicon compounds selected from (i) and (ii) described above in the presence of an acid. The acid may be, for example, a mineral acid such as hydrochloric, hydroiodic, sulphuric, nitric and phosphoric acid. When the organosilicon compound is a chlorosilane the acid may be generated in situ by hydrolysis of the chlorosilane or the reaction of the chlorosilane directly with hydroxyl groups on the clay surface. In step (A) it is only necessary that the acid be present in an amount sufficient to effect reaction of the organosilicon compound with the clay. Preferably, the acid catalyst provides a pH less than 6, more preferably a pH less than 3.

**[0019]** The temperature at which step (A) is conducted is not critical. Mixing of components in step (A) may conveniently be performed at room temperature with subsequent heating to facilitate treatment of the clay with the organosilicon compound. Clay treatment may be conducted, for example, at a temperature from 20°C up to the reflux temperature of the water-miscible solvent.

**[0020]** Step (A) may further include addition of a surfactant to facilitate treatment of the clay with the organosilicon compound. Suitable surfactants include, for example, anionic surfactants such as dodecylbenzene sulfonic acid, non-ionic surfactants such as polyoxyethylene(23)lauryl ether and  $(Me_3SiO)_2MeSi(CH_2)_3(OCH_2CH_2)_7OMe$  wherein Me is

methyl, and cationic surfactants such as N-alkyltrimethyl ammonium chloride.

[0021] In step (B) of the present method the aqueous suspension of the hydrophobic clay is contacted with a water-immiscible solvent to effect separation of the treated clay from the aqueous suspension. In a preferred method, steps (A) and (B) of the invention are sequentially conducted; however, the water-immiscible solvent may be added prior to, simultaneously with, or subsequently to the addition of the organosilicon compound of step (A). In the first two situations the treatment of the clay is accompanied by a phase separation in which the treated clay separates into the solvent phase.

[0022] For purpose of this invention any solvent immiscible with water can be employed. Suitable water-immiscible organic solvents include low molecular weight siloxanes such as hexamethyldisiloxane, octamethylcyclotetrasiloxane, diphenyltetramethyldisiloxane and trimethylsiloxy endblocked polydimethylsiloxane fluids. When a siloxane is employed as the treating agent, for example hexamethyldisiloxane or octamethylcyclotetrasiloxane, it may also act as the water-immiscible solvent if added in sufficient quantities, thus obviating the need for additional water-immiscible solvent. In addition, suitable water-immiscible organic solvents include aromatic hydrocarbons such as toluene and xylene; heptane, and other aliphatic hydrocarbon solvents; cycloalkanes such as cyclohexane; ethers such as amounts of materials used are shown in Table 1 below. In each of the Examples below the method of the present invention resulted in treatment and flocculation of the clay.

[0023] Clay was weighed into a 1 litre 3-neck round bottomed flask equipped with a mechanical stirrer and water condenser, and stirred at 200rpm whilst distilled water and isopropanol (IPA) were added. The mixture was then acidified with HCl before addition of the treating agent. After addition of the treating agent, the flask was heated to reflux for 40 minutes and allowed to cool before flocculation is attempted by addition of hexamethyldisiloxane. The flocculated clay is then washed using 1-3g  $\text{NaHCO}_3$  in 500g water followed by two further washes with 300g water.

Herein:

Treating agent

A =  $(\text{Me}_2\text{SiO})_4$

B = dimethyldichlorosilane

C =  $(\text{MeHSiO})_4$

D = 50:50 mixture of low mw linear and cyclic dimethylsiloxanes, approx. 15  $\text{mm}^2/\text{s}$

E = trimethyl terminated polymethylhydrogensiloxane, approx. 30  $\text{mm}^2/\text{s}$

F = hydroxy terminated polydimethylsiloxane (approx. 40  $\text{mm}^2/\text{s}$ )

G = n-octyltriethoxysilane

IPA = isopropyl alcohol

HMDS = hexamethyldisiloxane

[0024] Polestar 200R and Polestar 501 are highly refined kaolin clays calcined at 1100°C and 750°C respectively available from ECC International Limited.

[0025] Speswhite is a highly refined uncalcined kaolin clay available from ECC International Limited.

[0026] Polestar and Speswhite are trade marks of ECC International Limited.

Table 1

Treating agent	Wt. (g) treating agent	Clay (g)	Water (g)	Conc. HCl ( $\text{cm}^3$ )	IPA (g)	HMDS
Polestar 200R clay						
A	25.1	90.4	508.6	93	169.0	33
A	13.1	45.4	252.1	12	83.2	24
A	13.1	45.4	250.2	5	83.1	22
B	48.0	89.9	504.6	-	164.6	8.9
B	31.0	89.7	500.3	-	165.5	21.3
B	15.0	91.3	507.7	-	165.4	44.5
C	30.0	90.4	502.6	95	169.3	27.9
D	13.5	47.0	255.0	48	82.3	13
E	49.4	90.1	503.2	89	165.4	158

Table 1 (continued)

Treating agent	Wt.(g) treating agent	Clay (g)	Water (g)	Conc. HCl (cm <sup>3</sup> )	IPA (g)	HMDS
Polestar 200R clay						
F	46.0	90.2	512.0	90	165.5	2.0
G	45.1	92.4	506.1	92	165.9	128
Speswhite clay						
A	13.0	46.0	250.0	47	84.0	20.0
C	12.8	45.5	257.0	46	83.0	70
Polestar 501 clay						
A	12.9	45.5	252.7	47	83.2	28.2
C	13.0	45.4	250.2	45	82.9	50

[0027] The concept "comprising" where used herein is used in its widest sense to mean and to encompass the notions of "include", "comprehend" and "consist of".

### Claims

1. A method for preparing a hydrophobic clay, which method comprises:

(A) allowing a clay to be rendered hydrophobic by contacting an aqueous suspension of the clay with an organosilicon compound in the presence of an acid and a water-miscible solvent, wherein the organosilicon compound is selected from (i) organosilanes of formula  $R^1_aSiX_{4-a}$  wherein each  $R^1$  is independently selected from hydrogen and optionally substituted hydrocarbon radicals having 1 to 12 carbon atoms, each X is independently selected from halogen and alkoxy radicals having 1 to 12 carbon atoms, and  $a=1, 2$ , or  $3$ , and (ii) organosiloxanes comprising units of formula  $R^2_nSiO_{(4-n)/2}$  wherein each  $R^2$  is independently selected from hydrogen, hydroxy, and hydrocarbon radicals having 1 to 12 carbon atoms, at least 50 percent of the  $R^2$  substituents being hydrocarbon radicals, and  $n$  is 2 or 3, and  
 (B) contacting the clay suspension formed in step (A) with a water-immiscible solvent to effect separation of the hydrophobed clay from the suspension.

2. A method according to Claim 1 characterised in that the clay comprises calcined kaolin.

3. A method according to Claim 1 or 2 characterised in that the organosilicon compound is selected from  $(Me_2SiO)_4$ ,  $(MeHSiO)_4$ , dimethyldichlorosilane, n-octyltriethoxysilane,  $Me_3SiO(MeHSiO)_2SiMe_3$ , and  $HO(Me_2SiO)_yH$  wherein Me is methyl, z has an average value from 20 to 50 and y has an average value of from 10 to 15.

4. A method according to any preceding Claim characterised in that the aqueous suspension formed in step (A) has a pH less than 3.

5. A method according to any preceding Claim characterised in that the water-miscible solvent is isopropanol.

6. A method according to any preceding Claim characterised in that the water-immiscible solvent is a low molecular weight siloxane.

7. A method according to Claim 6 characterised in that the water-immiscible solvent is hexamethyldisiloxane.

8. A method according to any preceding Claim characterised in that the weight ratio of the water-immiscible organic solvent to clay is from 0.25:1 to 2:1.

9. A method according to any preceding Claim characterised in that steps (A) and (B) are performed sequentially.

10. A method according to any one of Claims 1 to 8 characterised in that steps (A) and (B) are performed substantially

simultaneously.

5

10

15

20

25

30

35

40

45

50

55



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 98 31 0402

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	FR 2 187 865 A (HUBER CORP J M) 18 January 1974 * claims 1,3-6,9,10 * * page 2, line 30 - page 6, line 32 * * examples 1-3 *	1-3,5	C09C1/42 C09C3/12 C08K9/06
A	FR 2 466 486 A (ENGLISH CLAYS LOVERING POCHIN) 10 April 1981 * claims 1-13 * * page 2, line 21 - page 5, line 14 * * examples 1-5 *	1-3	
A	EP 0 506 290 A (ECC INT LTD) 30 September 1992 * the whole document *	1-3	
A	EP 0 265 223 A (ECC AMERICA INC) 27 April 1988 * the whole document *	1-3	
A	FR 2 007 761 A (HUBER CORP J M) 9 January 1970 * the whole document *	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C09C
A	US 3 290 165 A (JOSEPH IANNICELLI) 6 December 1966		
A	US 3 227 675 A (JOHN G. PAPALOS) 4 January 1966		
A	GB 1 062 595 A (ESSO RESEARCH AND ENGINEERING COMPANY)		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 March 1999	Examiner Rigondaud, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 82 (P04C01)

BEST AVAILABLE COPY

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 31 0402

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-03-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2187865 A	18-01-1974	US 3834924 A	10-09-1974
		AT 325733 B	10-11-1975
		AT 510073 A	15-01-1975
		AU 467020 B	13-11-1975
		AU 5650173 A	05-12-1974
		CA 991924 A	29-06-1976
		GB 1430125 A	31-03-1976
FR 2466486 A	10-04-1981	DE 3036874 A	09-04-1981
		GB 2067535 A, B	30-07-1981
		US 4427452 A	24-01-1984
EP 0506290 A	30-09-1992	AU 646328 B	17-02-1994
		AU 1315392 A	01-10-1992
		GB 2254081 A, B	30-09-1992
		US 5244958 A	14-09-1993
EP 0265223 A	27-04-1988	US 4810578 A	07-03-1989
		AT 49991 T	15-02-1990
		AU 599708 B	26-07-1990
		AU 7957687 A	21-04-1988
		JP 63125576 A	28-05-1989
FR 2007761 A	09-01-1970	GB 1272287 A	26-04-1972
		US 3567680 A	02-03-1971
US 3290165 A	06-12-1966	NONE	
US 3227675 A	04-01-1966	NONE	
GB 1062595 A		NONE	

EPO FORM P/459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

BEST AVAILABLE COPY